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Photon harvesting glasses

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Abstract. Synthesis and photon harvesting properties of a series of lead phosphate glass-fullerene (C_{60}) composites and those of a group of Er^{+3} activated upconverting tellurite glasses are reported. On exposure to UV-VIS light, the glass-fullerene (C_{60}) composites were found to harvest the energy of the incident photons through creation of long lived charge separated Pb^{+3} holes and $C_{60}/(C_{60})_n$ anions in the media. The Er^{+3} activated tellurite glasses, on the other hand, were found to efficiently convert NIR photons to VIS light using the upconversion property of the activator ions. All these properties of the materials have shown prospect of their use in harvesting solar photons for photovoltaic energy conversion.

1. Introduction:

Efficient photon harvesting and their conversion to useful output are the two important areas of present day energy research [1- 4]. Photo-responsive materials those are stable, show reversibility in the photo-induced changes are most desired for such applications. In that respect a photo-responsive glass with suitable formation temperature seems to be the ideal candidate. Considering the fact that C_{60}-fullerene is photo-active and has interesting optoelectronic properties, we have synthesized a series of (zinc, lead)-phosphate glass-C_{60} composites. These composites show good photo-response upon UV-VIS irradiation. Viability of use of this photo-stored energy has been explored.

Another challenging area of light harvesting is the conversion of NIR part of solar spectrum to silicon solar cell sensitive UV-VIS light [4, 8]. Upconversion luminescence properties of rare earth activated materials are useful for this purpose. Efficient upconverting glasses seem to be appropriate for this job. Here enhancement of upconversion efficiency of two Er^{+3} activated tellurite glasses by generating Er^{+3} related nanocrystals in the matrix is also reported.

2. Experimental:

Different (Pb, Zn) phosphate glass - C_{60} composites were prepared by melting in controlled atmosphere. Samples were irradiated with UV-VIS light from a 125 watt Hg-lamp (Hanovia, USA) for a fixed time period, keeping the samples each time at a certain distance. Absorption spectra of the samples were measured at 300 K in a Shimadzu (Japan) UV-VIS absorption Spectrophotometer and post irradiation ESR spectra were recorded at 300 K in a (JEOL - JES RE1X) ESR Spectrometer. The 'I-V' characteristics were studied in a source-meter under illumination applying varying D. C. bias.

The Er^{+3} related two different nanocrystals dispersed tellurite glasses were prepared by melting two compositions (A) consisting of TeO_2, BaF_2, BaO, La_2O_3 and Er_2O_3 and the other (B) consisting of the above ingredients plus PbO, WO_3 as additional components. The nanocrystals were grown by ageing the respective glasses. The normal and the upconversion luminescence were recorded in a Perkin

Elmer spectrofluorimeter. For upconversion study a 976 nm fiber pig-tailed diode laser was used as an excitation source.

3. Results and Discussions:

3.1. Photoactive (Pb, Zn)- Phosphate glass - fullerene composites:
Figure 1 shows the picture of a sample of (Pb, Zn) - Phosphate glass - fullerene composite along with its FESEM micrograph. Figure 2, exhibits the steady state absorption spectrum of the composite at 300K in the λ - region 250-1250 nm. The spectrum exhibits a weak and broad absorption band in the

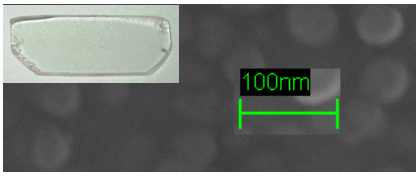


Figure 1. Picture of a sample of the composite along with its field emission scanning electron micrograph (FESEM).

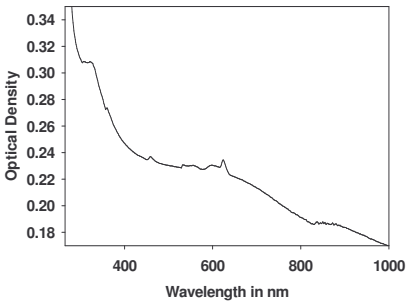


Figure 2. Absorption spectrum of C_{60} in the composite

λ-range 500-700 nm and another relatively less distinct broad band in the λ-range 800-900 nm. Considering the energy and weakness of transition of the high energy band one can easily recognize the band as the HOMO-LUMO forbidden transition of the incorporated C_{60} fullerene molecules, while the low energy band (800-900 nm) seems to originate from major fraction of C_{60} which have formed clusters $(C_{60})_n$, in the glass. FESEM study (Figure 1) of the composite also supports the above view.

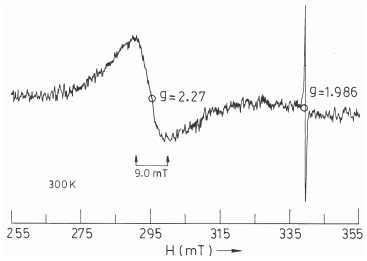


Figure 3. Photo-induced ESR spectrum of the composite.

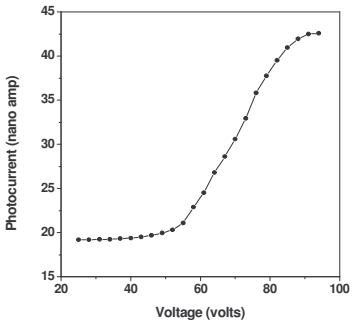


Figure 4. I-V characteristics of the composite.

Figure 3 shows ESR spectrum of the UV irradiated composite immediate after the cessation of irradiation. It exhibits two signals, in the field region 275 - 345 mT. The lower field resonance is broad having a peak to peak width $\Delta H_{pp} \approx 9$ mT and a 'g' factor = 2.27, while the higher field resonance is sharp with peak to peak width $\Delta H_{pp} = 0.3$ mT and 'g' = 1.986. We attribute the signal of the higher field region to the photo-generated C_{60}-anions. In case of a C_{60}^- anion 'g' and ΔH_{pp} values are reported to lie between 1.999-2.000 and 0.01-0.09 mT respectively. A lower value of 'g' in the present case possibly, suggests that the electron in the anion is largely delocalized: - a characteristics of the $(C_{60})_n^-$ cluster-anion. The values of the magnetic parameters (g = 2.27, $\Delta H_{pp} = 9.0$ mT) of the lower field resonance, on the other hand, suggest that it should be associated with a hole center of Pb^{+3} type (natural abundance of ^{204}Pb, ^{206}Pb, and ^{208}Pb together =79% and their I = 0). We suggest that the following photo-physical processes are involved in the generation of the above stated hole and trap.

$Pb^{+2} \xrightarrow{h\nu} Pb^{+3} + (-)$; $(C_{60}) + (-) \rightarrow (C_{60})^-$, $(C_{60})_n + (-) \rightarrow (C_{60})_n^-$

The I-V characteristics of the composite measured under illumination from a solar simulator (100 watts) is shown in Fig. 4. A current of maximum 40-45 nanoamps has been achieved under a bias of >70 volts. Threshold of the system is 55 volts.

3.2. Er-related nanocrystals dispersed upconverting tellurite glasses:

3.2.1. Microstructure and absorption spectra of the glasses:

X-ray and microstructural studies of the two glasses showed that the glass-A was dispersed with $Er_2Te_4O_{12}$ nanocrystals [8] while the glass-B was dispersed with Er_2WO_6 nanocrystals. Fig.5 shows the base-glass corrected absorption spectrum of the glass-A along with that of the glass B. The spectrum of the base glass of composition B (i.e. devoid of Er_2O_3) is also shown in the figure. In the first case, the spectrum exhibits a number of distinct strong absorption bands in the UV-VIS-NIR region due to transitions from the $^4I_{15/2}$ ground state to $^4G_{11/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ excited states of Er^{+3} while in the second case near UV bands of Er^{+3} are submerged.

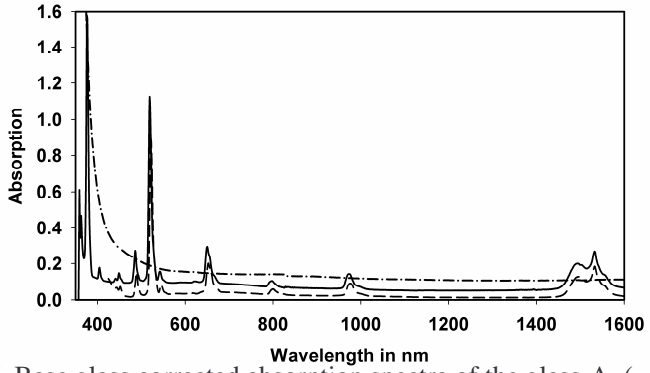
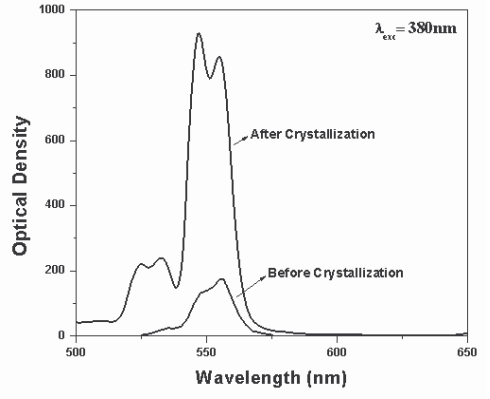
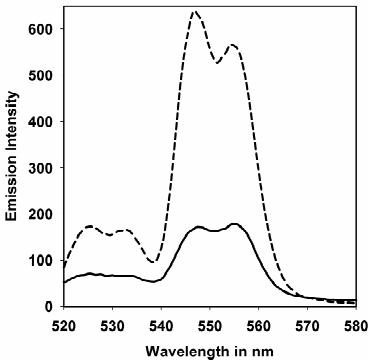


Figure 5. Base glass corrected absorption spectra of the glass-A, (____); similar spectrum of glass-B (--------); Spectrum of the base- glass of B (-.-.-.-.-.)

3.2.2. Effect of growth of nanocrystals on the normal and upconversion luminescence properties:

Figure 6a, shows the ($^2H_{11/2}$, $^4S_{3/2}$) → $^4I_{15/2}$ green luminescence spectra of Er^{+3} in the case of glass-B under 380 nm excitation before and after the growth of the $Er_2[WO_6]$ nanocrystals in the matrix, while the figure 6b shows the similar spectra before and after the growth of $Er_2Te_4O_{12}$ nanocrystals in the case of the glass-A.





6(a) 6(b)

Figure 6a and 6b, Green luminescence of Er^{+3} in the tellurite glass-B and in the tellurite glass-A respectively before and after the growth of respective nanocrystals under 380 nm excitation.

The enhancement of luminescence efficiency of Er^{+3} due to the growth of the respective nanocrystals is almost six times in the case of glass-B and 3.5 times in the case of glass-A. After the growth of the nanocrystals their respective band gaps possibly plays some important role in efficient excitation of the Er^{+3} ions in the glasses when the glasses are illuminated with near UV light (380 nm). Figure 7, shows the upconversion luminescence spectra of Er^{+3} in the Er_2WO_6 nanocrystals bearing tellurite glass upon excitation into the $^4I_{11/2}$ excited state of the ion with a 976 nm diode laser and its variation with the increase of laser power. Interestingly, the phenomenon of nanocrystal aided enhancement of efficiency of luminescence is observed also in the case of upconversion luminescence although the excitation energy in this case falls in the NIR region (976 nm).

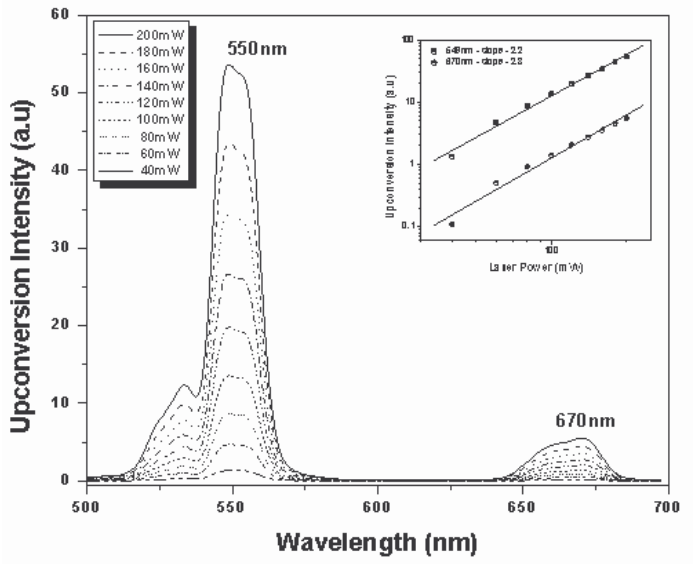


Figure 7. Upconversion luminescence of Er^{+3} in the glass-B, under 976 nm laser excitation.

A very strong upconversion green luminescence from Er^{+3} ions at 549 nm due its $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions is observed along with a weak ~ 670 nm ($F_{9/2} \rightarrow {}^4I_{15/2}$) red emission. Excitation - power dependence of the upconversion luminescence shows a linear bi-photonic relationship. A similar enhancement of efficiency is observed also in the case of the glass-A. Possible reason of such enhancement is increase in localized concentration of Er^{+3} after the growth of the nanocrystals. Before the growth of the nanocrystals ions were randomly distributed but in the crystals they are regularly distributed. Thus the glasses showed prospect of being used as solar NIR concentrator.

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